



Remediation of simulated aquatic sites contaminated with recalcitrant substrates by TiO₂/ozonation under natural sunlight

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ABSTRACT

The fates of four aquatic contaminants, namely the 2,4-dichlorophenoxyacetic acid herbicide (2,4-D), the bisphenol A endocrine disruptor (BPA), and the sodium butylnaphthalenesulfonate (BNS) and benzylidodecyldimethylammonium bromide (BDDAB) surfactants by the TiO₂-photoassisted ozonation (TiO₂/O₃/UV method) were investigated indoors under laboratory conditions (super-high-pressure Hg lamp) and outdoors under natural Sunlight. In laboratory experiments the TiO₂/O₃/UV methodology led to significant increases in degradation efficiency relative to ozonation (dark: O₃; or under UV light: O₃/UV) and to the TiO₂-photoassisted method of oxygenated dispersions (TiO₂/O₂/UV). Mineralizations of the substrates were monitored by total organic carbon (TOC) assays. The BDDAB surfactant, being most recalcitrant to biodegradation and to the TiO₂-photoassisted degradation, was mineralized efficiently by the TiO₂/O₃/UV method under natural Sunlight at relatively high concentrations of contaminants (1.0 mM) using a tubular-type photoreactor consisting of Pyrex glass tubes and a solar cell system that supplied the needed electrical power.

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1. Introduction

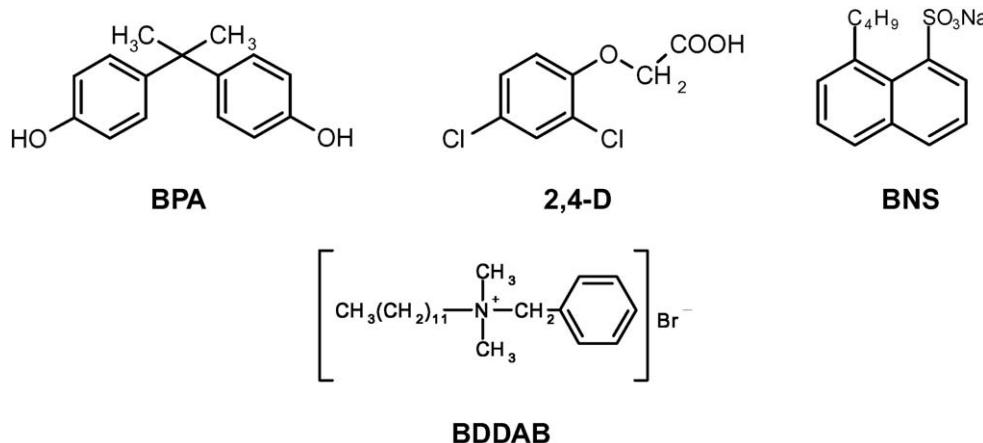
Organic contaminants often recalcitrant to biodegradation such as surfactants, endocrine disruptors, pesticides and herbicides necessitate either single technologies (e.g. ozonation, peroxidation, UV irradiation, Fenton) or more often integrated technologies (e.g. UV/O₃, UV/H₂O₂, photo-Fenton) for their degradation and ultimate mineralization to carbon dioxide. As a single methodology, TiO₂ photocatalysis has proven advantageous in remediation of contaminated wastewaters, although large-scale application remains somewhat expensive owing to the cost of photons and slow oxidation dynamics. Nonetheless, this single advanced oxidation technology can prove advantageous for relatively low contaminant loadings at the source of contamination even though complete mineralization may be attained but slowly.

Utilization of natural Sunlight to mineralize organic contaminants in wastewaters can substantially reduce running costs [1,2].

Earlier work has demonstrated the feasibility of using Sunlight and TiO₂ as the possible photocatalyst to photodegrade various organic pollutants such as bisphenol-A (BPA), 2,4-dichlorophenoxyacetic acid (2,4-D), the methylene blue dye (MB), and the benzenesulfonate (BS), dodecylbenzenesulfonate (DBS) and butylnaphthalene-sulfonate (BNS) surfactants as well as a complex commercial detergent [3–7]. Integrating the TiO₂-photoassisted methodology and ozonation can improve process efficiency in the treatment of contaminated aquatic sites through a combination of factors that leads to faster process dynamics [8–10].

In the present study we examined the degradation and mineralization of BPA, 2,4-D and the BNS and benzylidodecyldimethylammonium bromide (BDDAB) surfactants by exploring various methods, but most notably the combined TiO₂/ozonation methodology at the pilot plant scale outdoors using natural Sunlight and for comparison indoors at the laboratory scale using a super high-pressure Hg lamp as the light source.

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2. Experimental

2.1. Materials

TiO₂ was Degussa P-25 (surface area, *ca.* 53 m² g⁻¹; mean diameter, *ca.* 30 nm; composition: 87% anatase and 13% rutile). The BNS was obtained from the Kao Corporation, Japan (PELEX NBL). Reagent grade BPA was purchased from Tokyo Kasei Industries Co. Ltd., whereas BDDAB and 2,4-D were supplied by Wako Pure Chemical Industries. Co. Ltd. Ozone was produced from pure oxygen using an ozone generator (EcoDesign ED-OG-S1); dosage rate 0.2 g h⁻¹. All other chemicals were used as received.

2.2. Photodegradation procedures

Total organic carbon assays were performed on a Shimadzu TOC-5000A analyzer. In the laboratory experiments, the substrate solutions (1.0 mM, 50 mL) were transferred to a 127 mL Pyrex glass vessel containing TiO₂ subsequently irradiated with a 75 W super high-pressure Hg lamp (light irradiance, 3 mW cm⁻² at 360 nm; UV radiometer model UVR-36 from Topcon Co.). In solar experiments, the electric power for the reactor system, the pumps, the ozone generator, the radiometer and the computer was entirely supplied by a Sharp NE70H solar cell battery.

To examine the difference of reaction dynamics between the various methodologies, the solutions were treated under the following conditions: (i) TiO₂/O₂/UV system – the titanium dioxide was suspended in an aqueous solution of the substrates and purged with oxygen gas to saturation prior to UV light irradiation; (ii) O₃ system – O₃ gas was supplied by bubbling through the TiO₂-free solution under dark conditions; (iii) O₃/UV system – O₃ gas was supplied by bubbling through the TiO₂-free solution during the entire UV light irradiation period; and (iv) TiO₂/O₃/UV system – O₃ gas was supplied by bubbling in the aqueous TiO₂ suspension subjected to constant UV light (or sunlight) irradiation. The dispersions were initially sonicated for about 10 min to ensure a uniform dispersion, followed by magnetic agitation (stirrer) to obtain a satisfactory suspension and a uniform reacting mixture during the photooxidative processes.

In all experiments, various aliquots of the degraded solutions/suspensions were collected at fixed time intervals during the degradation/mineralization. Mineralization was assayed by monitoring the time profiles of loss of TOC in the solutions or dispersions. For the suspensions, TOC assays were performed after removal of the TiO₂ particles by centrifugation and filtration through an advanced 0.2 µm PTFE filter. The concentration of ozone in the water was determined by iodometric analyses, which in all cases was 25 ppm by keeping the O₃ flow constant throughout.

3. Results and discussion

3.1. Laboratory experiments

Oxidative degradation of the anionic BNS surfactant in aqueous solution was carried out by the four different (i–iv) procedures noted above. Time profiles in the change of TOC levels are reported in Fig. 1. Initial TOC levels before irradiation in the plots are those of solutions containing no metal-oxide particles, whereas the TOC levels at time = 0 min are those determined after addition of TiO₂ and after the sonication process, but before irradiation by the UV lamp or by the natural sunlight. The BNS surfactant was only slightly mineralized (*ca.* 18% TOC loss after 2 h of irradiation) by the TiO₂-photoassisted process, contrary to ozonation in the dark (method ii; about 20% TOC loss) and UV/ozonation processes (method iii); the latter caused TOC to decrease significantly more (~40% after 2 h). By contrast, addition of O₃ to the TiO₂-photoassisted process led to complete mineralization of the sulfonated surfactants after 1.5 h of irradiation clearly demonstrating the synergistic effect between TiO₂, O₃, and UV light.

The oxidative mineralization of the cationic BDDAB surfactant by ozonation (dark; O₃) and UV/ozonation (O₃/UV), by the TiO₂-photoassisted method in oxygenated media (TiO₂/O₂/UV) and by the combined TiO₂-photoassisted ozonation methodology (TiO₂/O₃/UV) is reported in Fig. 2. Only the latter TiO₂-photoassisted

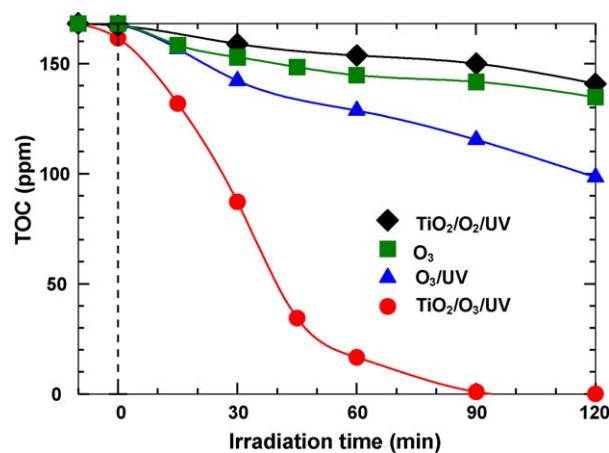


Fig. 1. Time profiles of TOC concentration changes in the TiO₂-photoassisted ozonation (TiO₂/O₃/UV) of the BNS surfactant in comparison to ozonation, UV/ozonation and UV-irradiated TiO₂ methods. Initial conditions: BNS, 1.0 mM, 100 mL; TiO₂ loading, 200 mg (2.0 g L⁻¹); O₃ concentration, 25 ppm; irradiation source, Hg lamp.

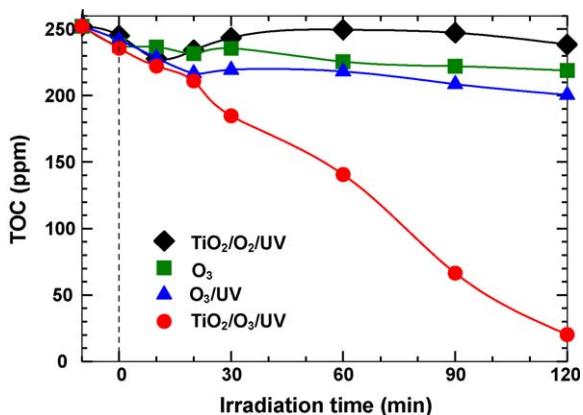


Fig. 2. Time profiles of the TOC concentration changes in the mineralization of the BDDAB surfactant under the same methods and conditions as those described in Fig. 1.

ozonation method led to near complete mineralization (ca. 92%) of this surfactant after 2 h of irradiation by a zero-order process.

There is no doubt that the surface charge of TiO₂ particles is positive in acidic media at pHs below the point of zero charge (pH_{pzc} ca. 6.7). Thus at a pH of 5.6 of the aqueous BDDAB solution adsorption of this cationic surfactant on the surface of TiO₂ was suppressed by the repulsive Columbic forces between the positively charged TiO₂ surface and the substrate. Accordingly, the TiO₂-photoassisted degradation of this surfactant was less favourable compared to the anionic surfactant. Nonetheless, simultaneous usage of both TiO₂ and ozone under UV light led to a significant oxidative mineralization of this cationic surfactant. A similar tendency was obtained for the oxidative degradation of 2,4-D and BPA when carried out under otherwise identical experimental conditions as illustrated by the results reported in Fig. 3a and b, respectively.

Clearly then, experimental results show unambiguously that significant mineralization takes place by the combined TiO₂/O₃/UV methodology as compared to either ozonation or UV/ozoneation and to the TiO₂-photoassisted process in oxygenated dispersions (TiO₂/O₂/UV).

The results displayed in Figs. 1–3 are best understood by considering all the possible oxidizing agents present in the solutions or dispersions. The strongly photooxidative •OH radical species generated according to reactions (1–10) no doubt attack the electron-rich functions in the various organic substrates. It is noteworthy that production of •OH radicals tends to be more effective in the presence of O₃ [9].

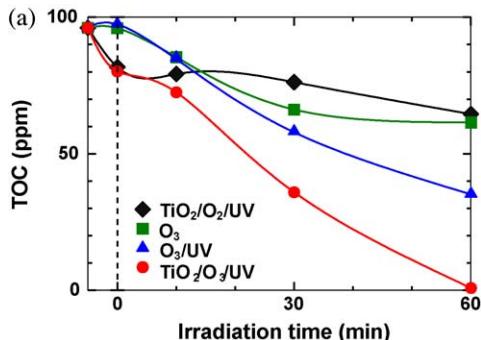
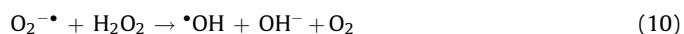


Fig. 3. Time profiles of the TOC concentration changes in the mineralization of (a) 2,4-D, and (b) BPA. Experimental methodologies and conditions are otherwise identical to those of Fig. 1.

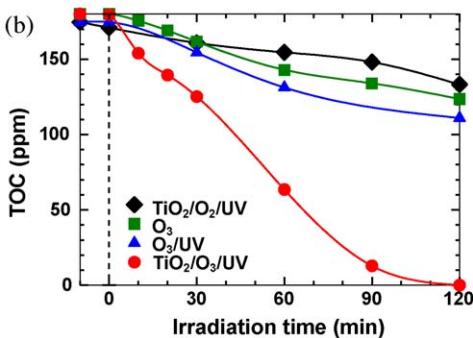


Subsequently, the strongly oxidative species of OH radicals formed on the TiO₂ surface attack the moieties having higher electron density such as aromatic ring, followed by the generation of the hydroxylated aromatic intermediates. The aromatic ring was then cleaved to form aldehyde and/or carboxylic acid derivatives by further photo-illumination. Finally, CO₂ gas was evolved and the TOC value in the degraded aqueous solution decreased. The experimental evidence by ESR-spin trapping technique and TOF-MS spectroscopic analysis has been published in our previous papers [11,12].

3.2. Natural sunlight outdoor experiments

Results from the laboratory experiments led us to examine the mineralization of BPA, 2,4-D and of the BNS and BDDAB surfactants outdoors under irradiation with natural sunlight using the combined TiO₂/O₃/UV method that proved most efficient under irradiation by the more traditional Hg lamp. To achieve this objective, we examined aqueous dispersions of substrates at a concentration of 1.0 mM, which is typically greater than the usual contaminant loadings discovered in natural wastewaters.

The experiments were performed with a photoreactor that consisted of 20 Pyrex glass tubes (inner diameter, 1.76 cm; length, 145 cm; total area subjected to sunlight irradiation, 5104 cm²) connected in series as illustrated in Fig. 4. A peristaltic pump (PR-KV2, Furue Science Co.) ensured the re-circulation of the 14 L reactant solution between the photoreactor and the O₃-bubbling tubes. As the reactor consisted of glass tubes, the reactant dispersion could be re-circulated at a relatively high flow rate (7.5 L min⁻¹) that provided turbulent flow conditions. The solar irradiance was measured every second with a radiometer at a wavelength of 360 nm. The data obtained were then integrated using a personal computer. As sunlight irradiance is intermittent during the day according to weather conditions, decrease of TOC during the course of mineralization is reported (Fig. 5) as a function



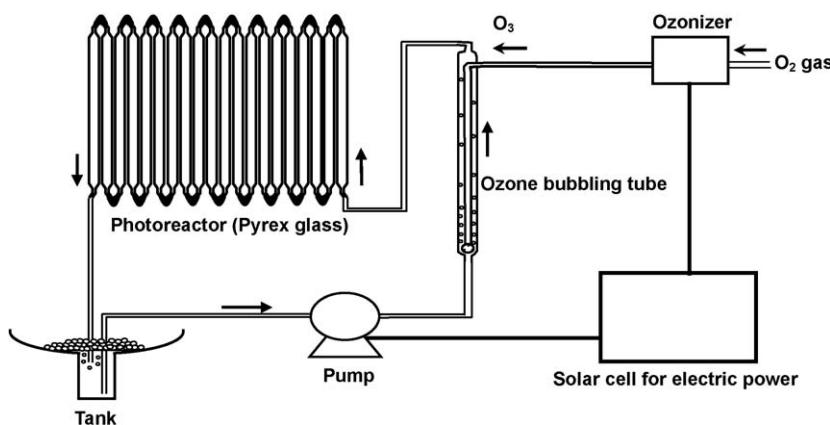


Fig. 4. Schematic illustration of the solar reactor system.

of accumulated sunlight energy (in units of kJ L^{-1}) incident on the photoreactor per liter of the solution as the variable, rather than against time. For instance, on a sunny day and at a solar irradiance of 3 mW cm^{-2} during 1 h of irradiation, the photoreactor harvests an accumulated energy of 4 kJ . Initially in the case of the surfactants, O_3 bubbling caused significant foaming of the reactant solution to appear in the tank. Accordingly, we used a stainless steel funnel-type receiver to hold the foam as depicted in Fig. 4. Note that the foaming action gradually disappeared as degradation of the surfactants proceeded.

The results of the solar mineralization of BPA, 2,4-D and of the two BNS and BDDAB surfactants by $\text{TiO}_2/\text{O}_3/\text{UV}$ (sunlight) are displayed in Fig. 5. Complete mineralization of the 2,4-D herbicide at a relatively high TiO_2 loading (2.0 g L^{-1}) and substrate concentration (1.0 mM) was achieved after only ca. 2 h of sunlight irradiation. By contrast, the BPA endocrine disruptor and the two surfactants BNS and BDDAB necessitated somewhat longer exposures ($>15 \text{ h}$) to natural sunlight to effect sufficient mineralization.

It was the goal of the present study to examine which of the four possible methodologies might be most efficient and thus the feasibility of mineralizing three different representative classes of contaminants found in wastewaters, and not the economics of a given process relative to others as many factors influence such estimates (e.g. initial capital costs, maintenance and labor costs,

cost of money, geographic location of photoreactor, intermittency of natural sunlight, and solar insolation among others). Nonetheless, Kopf et al. [13] have made a rough estimate of the energy consumed by a UV lamp and an ozone generator in laboratory experiments for the TiO_2 -photocatalyzed ozonation (herein the $\text{TiO}_2/\text{O}_3/\text{UV}$ method) of monochloroacetic acid and pyridine relative to the TiO_2 -photocatalyzed ($\text{TiO}_2/\text{O}_2/\text{UV}$) and UV/ozonation (O_3/UV) methods. Although the TiO_2 -photocatalyzed ozonation needed additional electrical energy for the ozone generator, the specific energy consumption for the photocatalyzed ozonation process was 3.5 times lower for the oxidation of monochloroacetic acid and 11 times lower for pyridine relative to the energy required for the TOC reduction by the $\text{TiO}_2/\text{O}_2/\text{UV}$ treatment methodology. Compared to TiO_2 -photocatalysis and UV/ozonation, the reduction in costs was approximately 20 and 6.5 times lower for monochloroacetic acid and pyridine, respectively, in favor of the $\text{TiO}_2/\text{O}_3/\text{UV}$ methodology. In the present study, the electrical power for the system, the peristaltic pump, the O_3 generator and the personal computer was entirely supplied by the solar cell whose energy was strictly obtained from sunlight. Note that any economic analysis would also have to take into account the sunlight-to-electrical power conversion efficiency as an additional factor. Regardless, the use of solar radiation as the energy source can significantly reduce running costs as only natural Sunlight is used. Moreover, the operating system depicted in Fig. 4 for remediation of contaminated wastewaters and similar contaminated sites can be utilized at locations far from any electrical network, not least of which the methodology is also favorable in terms of ecological considerations.

4. Conclusions

Laboratory experiments have demonstrated that irradiation of the combined TiO_2 -photoassisted ozonation process ($\text{TiO}_2/\text{O}_3/\text{UV}$) with a super high-pressure Hg lamp represents an efficient route toward the degradation and complete mineralization of water pollutants, particularly the non-biodegradable cationic surfactant(s). This combined methodology enhances the mineralization efficiency in comparison with those involving ozonation (dark), UV/ozonation, and the TiO_2/UV processes alone. The outdoor solar experiments further demonstrated that organic aquatic pollutants at relatively high concentrations can be mineralized easily and rapidly to carbon dioxide. Now that the feasibility has been demonstrated, future studies will explore larger scale solar photoreactors along with an examination of experimental optimal conditions (e.g. pH of reactant solution, re-circulation flow rates, TiO_2 loadings and O_3 dose).

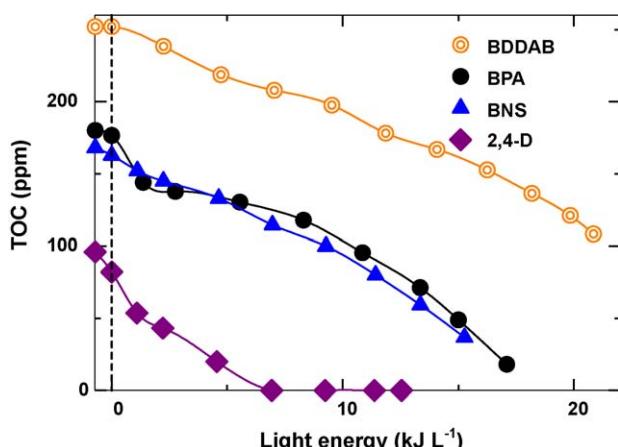


Fig. 5. Time profiles of TOC loss in the Sunlight-irradiated TiO_2 -photoassisted ozonation ($\text{TiO}_2/\text{O}_3/\text{UV}$) of the BNS, BDDAB, 2,4-D and BPA water pollutants. Initial concentrations, 1.0 mM ; volume of solution, 14 L ; TiO_2 loading, 28 g (loading, 2.0 g L^{-1}).

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